

# Characterization of the mixed axial ligand complex (4-cyanopyridine)(imidazole)(tetramesitylporphinato)iron(iii) perchlorate. Stabilization by synergic bonding

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> **ABSTRACT:** The reaction of  $[Fe(TMP)(OCIO_3)]$ , where TMP is the dianion of tetramesitylporphyrin, with a combination of a strong  $\pi$ -acceptor ligand and a  $\pi$ -donating imidazole can lead to the preparation of mixed-ligand complexes  $[Fe(Porph)(4-CNPy)(L)]^+$  where L is imidazole itself or 1-acetylimidazole and 4-cyanopyridine is the strong  $\pi$  acceptor ligand. The stability of the new mixed-ligand pair is the presumed result of synergic bonding between the two axial ligands. The molecular structure and other characterization of the new mixed axial ligand complex,  $[Fe(TMP)(4-CNPy)(HIm)]ClO_4$  is described. The axial ligands have a relative perpendicular arrangement with Fe–N(imidazole) = 1.945 Å and Fe– N(pyridine) = 2.021 Å. The average equatorial Fe–N<sub>p</sub> distance is 1.963 Å, which is consistent with the  $S_4$ -ruffled TMP core. Despite the relative perpendicular arrangement of axial ligands, the EPR spectrum of the complex is a rhombic signal and not a large  $g_{\text{max}}$  signal. The EPR g-values are  $g_1 = 3.05, g_2 = 2.07$ , and  $g_3 = 1.22$ . A quadrupole doublet was seen in the Mössbauer spectrum with an isomer shift of 0.197 mm/s and quadrupole splitting of 1.935 mm/s. Two crystalline forms of  $[Fe(TMP)(4-CNPy)(HIm)]ClO_4$ have been characterized; the two forms differ only in the solvent content of the lattice. Crystal data for form A: a = 15.432 (12) Å, b = 20.696 (2) Å, c = 19.970 (5) Å, and  $\beta = 99.256 (14)^{\circ}$ , monoclinic, space group  $P2_1/n$ , V = 6295 (2) Å<sup>3</sup>, Z = 4, formula FeCl<sub>3</sub>O<sub>4</sub>N<sub>8</sub>C<sub>69</sub>H<sub>69</sub>, 8397 observed data,  $R_1 = 0.086$ ,  $wR_2 =$ 0.210, refinement on  $F^2$ . Crystal data for form **B**: a = 15.267 (3) Å, b = 20.377 (6) Å, c = 19.670 (4) Å, and  $\beta = 98.14 (1)^\circ$ , monoclinic, space group  $P2_1/n$ ,  $V = 6058 (4) Å^3$ , Z = 4, formula  $C_{65.25}H_{60.5}Cl_{1.5}FeN_8O_4$ , 5464 observed data,  $R_1 = 0.096$ ,  $wR_2 = 0.112$ , refinement on F.

**KEYWORDS:** 

### **INTRODUCTION**

The electronic structures of the iron porphyrinates are rich and diverse. Such diversity includes, but is not limited to, a variety of oxidation states. Such richness is also mirrored the diversity of biological functions ranging from catalysis, electron transfer, to oxygen transfer and utilization [1].

For the bis-ligated iron(III) porphyrinates with two equivalent ligands, the effects of the axial ligand orientation are substantial and well understood. The absolute axial ligand orientation has been defined as the dihedral angle between the ligand plane and the plane defined by the donor atom, the iron and the porphyrinato nitrogen atom closest to the ligand (sometimes the Fe–N<sub>p</sub> bond direction is used instead). This angle is frequently called  $\phi$ . The relative ligand orientation is defined as the

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dihedral angle between the two axial ligand planes. Most such dihedral angles are close to either  $0^{\circ}$  or  $90^{\circ}$ ; these limiting forms are termed as the (relative) parallel or perpendicular orientation, respectively.

Changes in the absolute orientation of the two ligands can lead to the differing spin states of the iron with highspin, intermediate-spin and low-spin species resulting that are clearly related to the absolute ligand orientations [2, 3]. In addition for low-spin species, the relative orientation of the two axial ligands has substantial effects on the energies of the three lowest energy *d* orbitals [4–11].

We report in this paper strategies for the isolation and characterization of mixed axial ligand complexes of iron(III) porphyrinates, which to our knowledge have not been previously reported. We have used appropriately chosen imidazole and pyridine ligand pairs to accomplish this. In addition to their novelty, such mixed-ligand species are interesting because one can study both the orientation effects (particular orientation of the axial imidazole and pyridine with respect to the heme axes, and the relative orientation of the two ligand planes with respect to each other) and the crystal field effects (splitting of the *d* orbitals) of the axial ligands.

The major complex reported herein is [(imidazole) (4-cyanopyridine)(tetremesitylporphinato)iron(III)] perchlorate, [Fe(TMP)(4-CNPy)(HIm)][ClO<sub>4</sub>] [12]. Two crystalline forms of this complex have been isolated that differ only in solvent content. Their preparation and characterization are described here.

### **EXPERIMENTAL SECTION**

### **General information**

All reactions were performed under an argon atmosphere with Schlenk-ware and cannula techniques. All solvents were distilled under argon prior to use. Dichloromethane and hexane were distilled from CaH<sub>2</sub> and sodium/benzophenone, respectively. 4-Cyanopyridine was recrystallized from diethyl ether and imidazole was recrystallized from dichloromethane. Tetramesitylporphyrin was prepared by a modified version of the procedure published by Lindsey et al. [13] and iron was inserted into  $H_2TMP$  [12] by standard techniques [14]. [Fe(TMP)OClO<sub>3</sub>] was prepared as previously described [6]. *Caution*! These perchlorate salts can detonate spontaneously and should be handled only in small quantities; other safety precautions are also warranted. UV-vis spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. Mössbauer samples were prepared from ground single-crystal samples as mulls in Apiezon L grease, as previously described [7]. Mössbauer measurements were made on a constant acceleration spectrometer. The spectra were fitted with Lorentzian line shapes. Isomer shifts are quoted relative to metallic iron at room temperature

### Synthesis of [Fe(TMP)(4-CNPy)(HIm)] [ClO<sub>4</sub>]

At least two crystalline forms of [Fe(TMP)(4-CNPy) (HIm)]ClO<sub>4</sub> have been prepared by slight variation in crystallization procedures. Crystal form B was synthesized as follows: [Fe(TMP)OClO<sub>3</sub>] (30 mg, 0.032 mmol) and 4-CNPy (20 mg, 0.192 mmol) were placed in an argon-purged,  $15 \times 1.5$  cm test tube. Dichloromethane (2 mL) was added and the solution was stirred for 3 min. Imidazole (2.4 mg, 0.035 mmol) was added and stirred for an additional 3 min. The solution was then layered with 6 mL of hexane. Crystal form A was subsequently prepared in the following manner: [Fe(TMP)OClO<sub>3</sub>] (120 mg, 0.127 mmol) and 4-CNPy (79.5 mg, 0.763 mmol) were placed in a 25-mL Schlenk flask. Dichloromethane (~8 mL) was added and the solution was stirred for 10 min. The UV-vis (CH<sub>2</sub>CI<sub>2</sub>) spectrum (410, 534, 571.5 (sh) nm) is that of  $[Fe(TMP)(4-CNPy)_2][ClO_4]$  [6]. A dichloromethane solution of HIm (0.127 mmol) was added to the solution with syringe and stirred for an additional 20 min. A new UV-vis spectrum results (CH<sub>2</sub>CI<sub>2</sub>)  $\lambda_{max}$ : 414 (Soret), 546, 580 (sh) nm. The reaction mixture was transferred to four  $15 \times 1.5$  cm test tubes and layered with 15 mL of hexane. X-ray quality crystals formed after 4 days.

### X-ray structure determinations

Two black, crystalline forms of [Fe(TMP)(4-CNPy)-(HIm)]ClO<sub>4</sub> were examined on an Enraf-Nonius FAST area detector diffractometer at 127 K with graphitemonochromated MoKa radiation. Unit cell determination and data collection procedures with the area detector have been described previously [15]. A summary of cell constants and refinement results is given in Table 1; complete details are given in Table S1. Crystal form **B** was the first form investigated, but form A also confirms the preparation of the same mixed-ligand species. Slight variations in data collection instrument settings were used owing to differing crystal quality. Both data sets were corrected for Lorentz-polarization and absorption effects [16]. The structures were solved by Patterson methods with the SHELXS program [18]. During the course of structure solution and refinement, the solvent content of form **B** was found to be a single, partially occupied, methylene chloride molecule, located near an inversion center. This leads to the idealized formula  $[Fe(TMP)(4-CNPy)(HIm)]ClO_4 \cdot 1/4CH_2Cl_2$  for form **B**. Similarly, the formula for form A was established during structure solution as [Fe(TMP)(4-CNPy)(HIm)]  $ClO_4 \cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$ .

Least-squares refinement of the structural model for form **B** was carried out with a traditional refinement on F using the "observed" data, while that for form **A** was on  $F^2$  using all the unique, measured data including the reflections with negative intensities. In both structures, all nonhydrogen atoms were refined with atomic displacement factors. Hydrogen atoms were included as

| Molecule                                  | $\begin{array}{l} [Fe(TMP)(4\text{-}CNPy)(HIm)] \\ ClO_4 \ CH_2 Cl_2 \cdot 0.5 C_6 H_{14} \ Form \ \textbf{A} \end{array}$ | $[Fe(TMP)(4-CNPy)(HIm)]$ $ClO_4 0.25 CH_2Cl_2 Form B$                                  |
|---|--|--|
| formula                                   | C <sub>69</sub> H <sub>69</sub> Cl <sub>3</sub> FeN <sub>8</sub> O <sub>4</sub>  | C <sub>65.25</sub> H <sub>60.5</sub> Cl <sub>1.5</sub> FeN <sub>8</sub> O <sub>4</sub> |
| FW, amu                                   | 1236.57  | 1129.78  |
| <i>a</i> , Å                              | 15.4318 (12)   | 15.267 (3)   |
| <i>b</i> , Å                              | 20.696 (2)   | 20.377 (6)   |
| <i>c</i> , Å                              | 19.970 (5)   | 19.670 (4)   |
| β, deg                                    | 99.256 (14)  | 98.14 (1)  |
| $V, Å^3$                                  | 6295 (2)   | 6058 (4)   |
| space group                               | $P2_{1}/n$   | $P2_{1}/n$   |
| Ζ   | 4  | 4  |
| $D_c$ , g/cm <sup>3</sup>                 | 1.30   | 1.24   |
| μ, mm <sup>-1</sup>                       | 0.420  | 0.365  |
| radiation, MoK $\alpha$ , $\lambda$       | 0.71073 Å  | 0.71073 Å  |
| temperature, K                            | 127 (2)  | 127 (2)  |
| unique data                               | 16241  | 13051  |
| unique observed data $[I > 2\sigma(I)]$   | 8397   | 5464   |
| refinement method                         | Full-matrix least-squares on $F^2$   | Full-matrix least-squares on F   |
| final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.086, wR_2 = 0.210$ $R_1 = 0.096, wR_2 = 0.1$  |  |
| final <i>R</i> indices (all data)         | $R_1 = 0.168, wR_2 = 0.262$  |  |

**Table 1.** Brief crystallographic data and data collection parameters for the two forms of [Fe(TMP) (4-CNPy)(HIm)]ClO<sub>4</sub>

fixed, idealized contributors. The structures were then refined to convergence with the discrepancy indices listed in Table 1. Since the crystal and data quality of form **A** proved to be superior to that of form **B** and the structures are essentially identical, we report more details for form **A** herein. Complete sets of atomic coordinates, atomic displacement factors, bond distances, and bond angle tabulations for both **A** and **B** forms are given in the Supplementary Information.

# RESULTS

We have prepared the mixed axial ligand complex, [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub>, as a crystalline solid and have characterized it by single-crystal X-ray structure determinations and by Mössbauer and EPR spectroscopies. [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub> has been obtained in two crystalline forms which we call form **A** and form **B**; both have been characterized by single-crystal X-ray structure determinations. As we will later discuss, the two forms differ only in solvent content of the lattice. Hence we report details for form **A** only and summary information for form **B**. The molecular structure of form **A** is shown in Fig. 1 which also illustrates the atom labeling scheme used for all tables. The ORTEP diagram shows the interesting features of the molecule, *viz.*, that there are two nonequivalent ligands and that the two planar axial ligands have a relative perpendicular orientation. The actual dihedral angle between the two axial ligands is 85.4°. (In form B, this angle is 84.9°). The projection of the imidazole ligand plane onto the porphyrin plane makes an angle of 42° with the closest Fe–N<sub>p</sub> vector; the corresponding value for the pyridine ligand is 38.2°. These angles are frequently denoted by the symbol  $\phi$ .

Consistent with observations of [Fe<sup>III</sup>(TMP)L<sub>2</sub>]<sup>+</sup> derivatives having axial ligands with relative perpendicular orientations, the porphinato core exhibits an  $S_4$ -ruffling, which is illustrated in the formal diagram of Fig. 2. This figure displays the perpendicular displacements of each atom (in units of 0.01 Å) from the mean plane of the core. Also consistent with the ruffled core are the relatively short equatorial Fe-N<sub>r</sub> bond distances which average to 1.963 (10) Å. The axial (Fe<sup>III</sup>–N) distances are 2.021 (4) Å to the pyridine ligand and 1.945 (4) Å to the imidazole ligand. (For form  $\mathbf{B}$ , the axial (Fe<sup>III</sup>-N) distances arc 2.026 (9) Å and 1.933 (8) Å, respectively). The axial N–Fe–N angle is 177.6  $(2)^{\circ}$ ; the N<sub>ax</sub>-Fe-N<sub>p</sub> angles range from 88.4 (2) to 92.4 (2)°. Individual values of the bond distances and bond angles in form A are given in the Supporting Information and in the CIF file. Averaged values of the chemically equivalent bond distances and angles in the core are entered on Fig. 2. The dihedral angles between the peripheral mesityl groups and the porphinato core are



**Fig. 1.** ORTEP diagram of [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub> (Crystal form **A**). Thermal ellipsoids are drawn at the 50% probability level. Porphyrin hydrogen atoms have been omitted for clarity

reasonably close to perpendicular (77.0, 88.5, 89.5, and 84.1°). Equivalent drawings for form **B** are given in Figs S1 and S2 of Supplementary Information.

A second example of a mixed-ligand system, [Fe(TMP)(4-CNPy)(1-AcIm)]ClO<sub>4</sub>, has also been obtained as a solid-state species but is less definitively characterized than the unsubstituted imidazole derivative. A combination of relatively poor crystal specimens and solvent disorder severely limit the quality of the structure determination [19]. However, the structural results are reasonably interpreted in terms of a mixed-ligand species with all structural features similar to those observed for the two forms of [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub>.

Mössbauer spectroscopic measurements have been made on form **A** of [Fe(TMP)(4-CNPy)-(1-AcIm)] ClO<sub>4</sub> and on [Fe(TMP)(4-CNPy)(1-AcIm)]ClO<sub>4</sub>. The Mössbauer spectrum of polycrystalline form **A** taken at 170 K is shown in Fig. 3. Form **A** has a quadrupole doublet with a splitting ( $\Delta E_q$ ) of 1.935 (8) mm/s and an isomer shift ( $\delta$ ) of 0.197 (7) mm/s. The Mössbauer parameters for [Fe(TMP)(4-CNPy)(1-AcIm)]ClO<sub>4</sub> are 1.82 (4) mm/s and an isomer shift of 0.18 (3). See Fig. S3 of the Supporting Information.

## DISCUSSION

Although there are a number of mixed-ligand species of the general form  $[Fe^{III}(Porph)(L)(X)]$ , where X is an anionic ligand and L a neutral nitrogen donor, there are to our knowledge no reports of the preparation of species of the general form  $[Fe^{III}(Porph)(L)(L')]^+$  where L and L' are different neutral donors. The reaction of iron(III) porphyrinates with neutral axial nitrogen donors, L, has



**Fig. 2.** Formal diagram of the porphinato core in [Fe(TMP) (4-CNPy)(HIm)]ClO<sub>4</sub> for form **A** displaying displacement of each unique atom from the 24-atom mean plane. All displacements are given in units of 0.01 Å. Negative values of atom displacements are towards the imidazole ligand. Also entered on the diagram are the averaged values of all bond distances and angles of the core. The orientations of the two planar ligands with respect to core atoms are also displayed

been long known to lead to six-coordinate complexes, [Fe<sup>III</sup>(Porph)L<sub>2</sub>]ClO<sub>4</sub>:

$$[\text{Fe}^{\text{III}}(\text{Porph})(\text{OCIO}_3)] + L \xleftarrow{k_1} [\text{Fe}^{\text{III}}(\text{Porph})L(\text{OCIO}_3)] + L \xleftarrow{k_2} [\text{Fe}^{\text{III}}(\text{Porph})L_2] \text{CIO}_4$$
(1)



**Fig. 3.** Mössbauer spectrum of [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub> (Crystal form **A**) at 170 K and in a field of 2.2 kG perpendicular to the  $\gamma$  beam. The solid line is a Lorentzian fit with parameters given in the text with a quadrupole splitting  $\Delta E_q = 1.935$  mm/s and an isomer shift  $\delta$  of 0.197 mm/s

For any given ligand L, the first binding constant,  $K_1$ , is generally much smaller than the second  $(K_2)$  such that typically only  $\log \beta_2$  (K<sub>1</sub>K<sub>2</sub>) values can be measured [20, 21]. For neutral nitrogen donors the magnitude of the binding constant  $\beta_2$  is known to vary over a number of orders of magnitude and is also generally related to ligand pK<sub>a</sub> [20, 21]. In general, the differing values of binding constants suggest that for any arbitrarily chosen pair of potential ligands, one member of the ligand pair will have a much higher affinity for the iron(III) center that the other and the reaction will lead to the preparation of one of the possible bis-symmetrically ligated complexes. In particular, the binding constants for 4-cyanopyridine with iron(III) porphyrinates are known to be quite small, on the order of 108 smaller than imidazoles in DMF [21] and a 4-cyanopyridine ligand might thus be expected to be readily supplanted by almost any other neutral nitrogen donor.

However, our prior synthetic and structural work and that of others shows that there are large differences in the bonding characteristics of neutral nitrogen ligands ranging from strong  $\pi$ -donating to  $\sigma$ -donating to strong  $\pi$ -accepting character. Moreover, these differences have real effects on the electronic structure of the iron(III) center as revealed by EPR and Mössbauer spectroscopy in this work. Our strategy in the investigation of possible mixed-ligand species was to make use of the (expected) synergic bonding characteristics of differing axial ligands. In this study we used a  $\pi$ -accepting (4-cyanopyridine) and a  $\sigma$ - and  $\pi$ -donating (imidazole) combination. We first allowed up to two 4-CNPy ligands to bind to the iron(III) porphyrinate by using a modestly high concentration of that ligand in concentrated solution, followed by adding only one equivalent of the imidazole, which we hoped would thus only replace one of the 4-CNPy ligands. Clearly this strategy worked to produce the mixed-ligand complex.

The crystal structure determinations of the two forms of [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub> and the preliminary results for [Fe(TMP)(4-CNPy)(1-AcIm)]ClO<sub>4</sub> clearly demonstrate that ferric porphyrinates with mixed, neutral nitrogen ligands can be prepared as solid-state species. Indeed, the relative perpendicular orientation of the mixed axial ligands is that expected for such a synergic  $\pi$ -bonding ligand pair where the  $\pi$ -accepting ligand interacts with the filled  $d_{xz}$  orbital and the  $\pi$ -donating ligand with the orthogonal, half-filled  $d_{yz}$  orbital.

UV-vis spectra and solution EPR spectra, taken under conditions as similar to our preparative reaction conditions as possible, provides evidence that a mixed-ligand species exists to a significant extent in solution. The spectra of solutions of [Fe(TMP)(OClO<sub>3</sub>)] containing, respectively, 10 equivalents of 4-CNPy, 10 equivalents of 4-CNPy and 1 equivalent of imidazole, or 10 equivalents of imidazole per equivalent of iron(III) are shown in Fig. 4. The figure clearly shows that the spectrum of the solution containing both 4-CNPy and imidazole is not simply the sum of the two end species, suggesting the presence of a significant concentration of the mixed-ligand species in solution. The fact that any mixed-ligand complex forms at all in solution is remarkable given that the overall equilibrium constant ( $\beta_2$ ) for 4-CNPy or imidazole with [Fe(TMP)  $(OClO_3)$ ] differs by up to eight orders of magnitude.

The structural features of [Fe(TMP)(4-CNPy)(HIm)] ClO<sub>4</sub> are those generally expected for a low-spin iron(III) porphyrinate. The average Fe–N<sub>p</sub> distance of 1.963 (10) Å (form **A**) or 1.964 (12) Å (form **B**) are within the range of values observed for derivatives with significantly S<sub>4</sub>-ruffled cores and the magnitude of the ruffling is within the range observed previously for Fe<sup>III</sup>TMP derivatives [22].

We tabulate, for comparison, selected structural parameters for the known low-spin derivatives with at least one imidazole or pyridine as axial ligand in Table 2. The absolute orientation of the pyridine ligand ( $\phi = 38.2^\circ$ )



**Fig. 4.** Electronic spectra of a  $9.6 \times 10^{-6}$  M (300–500 nm) or  $1.28 \times 10^{-3}$  M (480–800 nm) CHCl<sub>3</sub> solutions of [Fe(TMP)(OClO<sub>3</sub>)] containing, respectively, 10 equivalents of 4-CNPy(...), 10 equivalents of imidazole (—), or 10 equivalents of 4-CNPy and 1 equivalent of imidazole (---), per equivalent of iron(III)

| Complex  | Fe–Np <sup>a</sup>      | Fe–N <sup><i>a,b</i></sup> <sub><i>ax</i></sub> | $\Phi^c$    | Relative orient <sup>c,d</sup>            | Porphyrin core conformation | EPR type          | Ref. |
|--|-------------------------|---|-------------|---|-----------------------------|-------------------|------|
| [Fe(TMP)(1,2-Me <sub>2</sub> HIm) <sub>2</sub> ]ClO <sub>4</sub> | 1.937 (12)              | 2.004 (5)<br>2.004 (5)                          | 44<br>44    | 89  | S <sub>4</sub> -ruffled     | NR <sup>e</sup>   | 23   |
| [Fe(TPP)(2-MeHIm) <sub>2</sub> ]ClO <sub>4</sub>                 | 1.970 (4)               | 2.010 (4)<br>2.015 (4)                          | 33<br>32    | 89  | S <sub>4</sub> -ruffled     | $g_{\max}$        | 24   |
| $[Fe(T2,6Cl_2PP)(1-VinIm)_2]ClO_4^{f}$                           | 1.972 (6)               | 1.968 (4)<br>1.976 (4)                          | 5<br>14, 20 | 6<br>76                                   | S <sub>4</sub> -ruffled     | rhombic $g_{max}$ | 4    |
| [Fe(TPP)(1-MeIm) <sub>2</sub> ]ClO <sub>4</sub>                  | 1.982 (11)              | 1.970 (3)<br>1.978 (3)                          | 32<br>22    | 10  | S <sub>4</sub> -ruffled     | rhombic           | 25   |
| [Fe(TMP)(1-MeIm) <sub>2</sub> ]ClO <sub>4</sub> <sup>h</sup>     | 1.987 (1)<br>1.988 (20) | 1.965 (3)<br>1.975 (3)                          | 42<br>23    | $\begin{array}{c} 0^g \\ 0^g \end{array}$ | planar                      | rhombic           | 6    |
| [Fe(TPP)(HIm) <sub>2</sub> ]Cl                                   | 1.989 (8)               | 1.957 (5)<br>1.991 (5)                          | 39<br>18    | 57  | S <sub>4</sub> -ruffled     | NR <sup>e</sup>   | 26   |
| [Fe(Proto IX)(1-MeIm) <sub>2</sub> ]                             | 1.990 (16)              | 1.966 (5)<br>1.988 (5)                          | 16<br>3     | 13  | S <sub>4</sub> -ruffled     | NR <sup>e</sup>   | 27   |
| [Fe(TPP)(tMU) <sub>2</sub> ]SbF <sub>6</sub>                     | 1.992 (5)               | 1.983 (4)                                       | 22          | $0^g$                                     | planar                      | rhombic           | 8    |
| [Fe(TPP)(cMU) <sub>2</sub> ]SbF <sub>6</sub> <sup>h</sup>        | 1.996 (10)              | 1.967 (7)<br>1.979 (7)                          | 29<br>15    | $\begin{array}{c} 0^g \\ 0^g \end{array}$ | planar<br>planar            | rhombic           | 8    |
| [Fe(TPP)(HIm) <sub>2</sub> ]Cl·H <sub>2</sub> O <sup>h</sup>     | 1.993 (7)               | 1.964 (3)<br>1.977 (3)                          | 41<br>6     | $\begin{array}{c} 0^g \\ 0^g \end{array}$ | planar                      | rhombic           | 28   |
| [Fe(TPP)(CuIm) <sub>2</sub> ]+                                   | 2.00 (3)                | 1.98 (1)  | 7           | 9   | S <sub>4</sub> -ruffled     | NR <sup>e</sup>   | 29   |
| [Fe(TPP)(4-CNPy)2]ClO4   | 1.952 (7)               | 2.008 (4)<br>1.997 (4)                          | 35<br>36    | 89  | S <sub>4</sub> -ruffled     | axial             | 9    |
| [Fe(TMP)(4-CNPy) <sub>2</sub> ]ClO <sub>4</sub>                  | 1.961 (6)               | 2.001 (5)<br>2.021 (6)                          | 44<br>43    | 90  | S <sub>4</sub> -ruffled     | axial             | 10   |

Table 2. Summary of structural parameters and EPR for low-spin six-coordinate iron(iii) imidazole and pyridine derivatives

|  |            |  | inueu)       |       |                         |                 |              |
|--|------------|--|--------------|-------|-------------------------|-----------------|--------------|
| [Fe(TMP)(3-EtPy) <sub>2</sub> ]ClO <sub>4</sub>                  | 1.964 (4)  | 1.989 (4)<br>2.002 (4)                 | 44<br>44     | 90    | S <sub>4</sub> -ruffled | $g_{\max}$      | 10           |
| [Fe(TMP)(3-ClPy) <sub>2</sub> ]ClO <sub>4</sub>                  | 1.968 (7)  | 2.006 (7)<br>2.018 (7)                 | 42<br>29     | 77    | S <sub>4</sub> -ruffled | $g_{\max}$      | 10           |
| [Fe(TMP)(4-NMe <sub>2</sub> Py) <sub>2</sub> ]ClO <sub>4</sub>   | 1.964 (10) | 1.978 (4)<br>1.989 (4)                 | 42<br>37     | 79    | S <sub>4</sub> -ruffled | $g_{\rm max}$   | 6            |
| [Fe(OEP)(4-NMe <sub>2</sub> Py) <sub>2</sub> ]ClO <sub>4</sub>   | 2.002 (4)  | 1.995 (3)                              | 36           | $O^g$ | planar                  | rhombic         | 6            |
| [Fe(TPP)(Py) <sub>2</sub> ]ClO <sub>4</sub>                      | 1.982 (6)  | 2.001 (5)<br>2.005 (5)                 | 38<br>34     | 86    | S <sub>4</sub> -ruffled | $g_{\max}$      | 30           |
| tri-[Fe(OEP)(3-ClPy) <sub>2</sub> ]ClO <sub>4</sub> <sup>i</sup> | 1.995 (6)  | 2.031 (2)                              | 41           | $0^g$ | planar                  | NR <sup>e</sup> | 2            |
| [Fe(TMP)(4-CNPy)(HIm)]ClO <sub>4</sub> <sup><i>j</i></sup>       | 1.963 (10) | 1.954 (4) (Im)<br>2.021 (4) (Py)       | 42<br>38     | 85    | S <sub>4</sub> -ruffled | rhombic         | this<br>work |
| [Fe(TMP)(4-CNPy)(HIm)]ClO <sub>4</sub> <sup>k</sup>              | 1.964 (8)  | 1.933 (8) (Im)<br>2.026 (9) (Py)       | 44<br>41     | 85    | S <sub>4</sub> -ruffled | NR <sup>e</sup> | this<br>work |
| [Fe(OEP)(1-MeIm) <sub>2</sub> ]+                                 | 2.004 (2)  | 1.975 (2)                              | 20           | $O^g$ | planar                  | NR              | 31           |
| paral-[Fe(TMP)(5-MeHIm) <sub>2</sub> ]ClO <sub>4</sub>           | 1.983 (4)  | 1.978 (6)<br>1.961 (5)                 | 20<br>10     | 30    | S <sub>4</sub> -ruffled | rhombic         | 11           |
| paral-[Fe(TMP)(5-MeHIm) <sub>2</sub> ]ClO <sub>4</sub>           | 1.981 (5)  | 1.980 (5)<br>1.985 (5)                 | 12<br>14     | 26    | planar                  | rhombic         | 11           |
| <i>perp</i> -[Fe(TMP)(5-MeHIm) <sub>2</sub> ]ClO <sub>4</sub>    | 1.981 (7)  | 1.957 (6)<br>1.973 (6)                 | 30<br>40     | 76    | S <sub>4</sub> -ruffled | $g_{\max}$      | 11           |
| [Fe(TPP)(5-MeHIm) <sub>2</sub> ]Cl                               | 2.008 (2)  | 1.975 (2)                              | 3.1          | 0     | planar                  | rhombic         | 32           |
| [Fe(TPP)(5-MeHIm) <sub>2</sub> ]Cl                               | 2.002 (2)  | 1.987 (3)                              | 4.6          | 0     | planar                  | rhombic         | 32           |
| paral-[Fe(OMTPP)(1-MeIm) <sub>2</sub> ]Cl                        | 1.990 (2)  | 1.975 (2)<br>2.016 (2)                 | 13<br>6      | 19    | S <sub>4</sub> -saddled | rhombic         | 33           |
| perp-[Fe(OMTPP)(1-MeIm) <sub>2</sub> ]Cl                         | 1.969 (7)  | 1.982 (10)<br>1.982 (10)               | 29<br>61     | 90    | S <sub>4</sub> -saddled | $g_{\max}$      | 33           |
| [Fe(OETPP)(1-MeIm) <sub>2</sub> ]Cl                              | 1.970 (7)  | 1.976 (3)<br>1.978 (3)                 | 10<br>7      | 73    | S <sub>4</sub> -saddled | $g_{\max}$      | 33           |
| [Fe(OETPP)(2-MeHIm) <sub>2</sub> ]+                              | 1.974 (9)  | 2.09 (2)<br>2.09 (2)                   | 14<br>14     | 90    | S <sub>4</sub> -saddled | $g_{\max}$      | 34           |
| [Fe(OETPP)(4-Me <sub>2</sub> Py) <sub>2</sub> ]Cl                | 1.951 (5)  | 1.984 (5)<br>2.015 (6)                 | 9<br>29      | 70    | S <sub>4</sub> -saddled | $g_{\max}$      | 34           |
| [Fe(OEP)(2-MeHIm) <sub>2</sub> ]Cl                               | 1.974 (4)  | 1.998 (2)<br>2.012 (2)                 | 40.8<br>43.4 | 87.6  | S <sub>4</sub> -ruffled | NR              | 35           |
| [Fe(TiPrP)(BzHIm) <sub>2</sub> ]+                                | 1.915 (5)  | 2.070 (5)                              | 45<br>44     | 90    | S <sub>4</sub> -ruffled | axial           | 36           |
| [Fe(TiPrP)(HIm) <sub>2</sub> ]+                                  | 1.938 (3)  | 1.993 (3)                              | 45<br>45     | ~90   | S <sub>4</sub> -ruffled | axial           | 36           |
| [Fe(TpivPP)(NO <sub>2</sub> )(HIm)]                              | 1.970 (4)  | 2.037 (10) (Im)<br>1.949 (10)<br>(NO2) | 16<br>37     | 69    | S <sub>4</sub> -ruffled | rhombic         | 37           |
| [Fe(TPP)(CN)(Py)]  | 1.970 (14) | 2.075 (3) (Py)                         | 40           |       | S <sub>4</sub> -ruffled | NR              | 38           |
| [Fe(TPP)(NCS)(Py)]   | 1.988 (9)  | 2.082 (3) (Py)<br>1.942 (4)<br>(NCS)   | 39           | _     | S <sub>4</sub> -ruffled | NR              | 39           |
| $[Fe(TPP)(N_3)(Py)]$   | 1.989 (6)  | 2.089 (6) (Py)<br>1.925 (7) (N3)       | 40           | 10    | S <sub>4</sub> -ruffled | NR              | 40           |

 Table 2. (Continued)

<sup>*a*</sup>Values in Å. <sup>*b*</sup>All independent axial distances are listed. <sup>*c*</sup>Values in degrees. <sup>*d*</sup>Dihedral angle between pair of axial ligands. <sup>*c*</sup>Not reported. <sup>*f*</sup>Disordered structure with relative parallel and perpendicular imidazoles. <sup>*s*</sup>Value of 0° required by symmetry. <sup>*h*</sup>Two independent molecules. <sup>*i*</sup>Triclinic form at 100K. <sup>*j*</sup>Form A. <sup>*k*</sup>Form B.

is within the range  $(24^{\circ}-45^{\circ})$  apparently required to form low-spin pyridine complexes. The absolute orientation of imidazole ligands in observed in low-spin complexes encompasses the entire possible range of 0°-45° and thus no particular absolute orientation is needed to form a lowspin imidazole complex (even with an S<sub>4</sub>-ruffled core). Thus there appears to be no steric constraints on either the absolute or relative imidazole orientation in order to form the low-spin complex [Fe(TMP)(4-CNPy)(HIm)] ClO<sub>4</sub>. We therefore believe that the relative perpendicular orientation of the imidazole and pyridine ligands in lowspin [Fe(TMP)(4-CNPy)(HIm)]ClO<sub>4</sub> are the result of bonding considerations and are not required by steric considerations. The relative perpendicular orientation is in agreement with the bonding requirements of the  $\pi$ -acceptor ligand which requires a filled orbital ( $d_{xz}$ ) and the  $\pi$ -donor ligand which interacts with the orthogonal half-filled orbital  $(d_{yz})$ .

Axial bond distance comparisons are also consistent with the idea that the relative ligand orientation is controlled by bonding. The axial Fe–N(imidazole) distance of 1.945 (4) Å is shorter than that observed in any bis-imidazole iron(III) derivative (Table 2), while the axial Fe–N(pyridine) distance of 2.021 (4) Å is as long as or longer than the Fe–N(pyridine) distances observed in the bis-pyridine derivatives. The short Fe–N(imidazole) distance is most consistent with very strong  $\pi$ -bonding between the iron(III) and imidazole. The Fe–N(imidazole) distance is also much shorter than the 2.068 (4) Å distance found for the five-coordinate high-spin complex [Fe(OEP)(2-MeHIm)]ClO<sub>4</sub> where strong axial bonding might be expected [42].

Although we have found and characterized two different crystalline forms of [Fe(TMP)(4-CNPy)(HIm)] ClO<sub>4</sub>, it is to be noted that the crystal structure, as well as the molecular structure, of both forms are quite similar. The cell packing diagrams for form **A** and form **B** (see Fig. 5) show that the packing of [Fe(TMP)(4-CNPy) (HIm)]<sup>+</sup> cations is essentially identical even though the solvent content in the two lattices clearly requires different cell volumes. Thus the two forms of [Fe(TMP) (4-CNPy) (4-CNPy)(HIm)]ClO<sub>4</sub> represent an additional set of cases of lattice packing dominated by the large metalloporphyrin species [43–46].

The Mössbauer spectrum of polycrystalline form **A** taken at 170 K is shown in Fig. 3. The spectrum illustrates a doublet with a quadrupole splitting of  $\Delta E_q = 1.935$  (9) mm/s and an isomer shift  $\delta$  of 0.189 (7) mm/s. The isomer shift is similar to values reported for other low-spin ferric hemes [5, 6, 10, 47]. Quadrupole splitting values less than ~1.75 mm/s are typical for low-spin iron(III) porphyrinates with axial ligands in the perpendicular orientation and a "pure"  $(d_{xy})^2(d_{xz}, d_{yz})^3$  ground state [5, 6, 10], while values greater than ~2.00 mm/s are typical for species with relative parallel orientation [5, 6]. With a quadrupole splitting value for form **A** in the middle (between) of the two limiting set of values, this is consistent with an

interesting and possibly distinctive ground state. A final system with two strong  $\pi$ -accepting ligands ([Fe(TPP) (4-CNPy)<sub>2</sub>]ClO<sub>4</sub>) has a quadrupole splitting value of 0.65 mm/s and an axial EPR spectrum [9].

EPR spectra of low-spin bis-ligated iron(III) porphyrinates have been shown to be particularly informative about the electronic structure. The relative energies of the three *d*-orbitals lowest in energy can be determined from the EPR g-values utilizing the Taylor formulation [48, 49]. Moreover, the EPR spectral type provides additional information. The observed type of EPR spectrum for all complexes listed in Table 2 are also given in the table when the spectrum has been measured. When the two planar axial ligands have a relative parallel orientation, rhombic spectra, with three distinct g-values, are observed. This is the result of a modest energy difference between the  $d_{xy}$  and  $d_{yz}$  orbitals since both axial ligands interact with only one of the two. However, when the two axial ligands planes have a dihedral angle close to 90°, i.e. a relative perpendicular orientation, a spectral type called  $g_{max}$  is observed. In this case, the two d orbitals interact more or less equivalently with the perpendicularly aligned ligands, leading to a very small energy gap between the  $d_{xy}$  and  $d_{xz}$  orbitals. A third type, with two strong  $\pi$ -acceptor ligands such as isocyanides, leads to an axial spectrum being observed. This is the result of the  $d_{xy}$  orbital becoming the highest energy orbital of the three  $t_{2g}$  orbitals as the energies of two  $d_{\pi}$ orbitals are lowered because of the interaction with the  $\pi$ -acceptor ligands. We know of no case where a relative orientation of the two planar ligands leads to a rhombic EPR spectrum.

What type of EPR spectrum will [Fe(TMP)(4-CNPy) (HIm)]ClO<sub>4</sub> display? From the data of Table 2, two distinct possibilities can be envisioned. The perpendicular orientation of the two ligands in [Fe(TMP)(4-CNPy) (HIm)]ClO<sub>4</sub> suggests that a strong  $g_{max}$  spectrum would be expected. However, the expected synergic bonding of the two ligands, one  $\pi$  accepting and one  $\pi$  donating, leads to a different prediction. The axial ligands and the metal  $d_{xy}$  and  $d_{xz}$  orbitals are 90° apart. Thus, one ligand (the  $\pi$  acceptor) will interact with the filled  $d_{xx}$  orbital and the other ligand (the  $\pi$  donor) will interact with the singly occupied  $d_{yz}$  orbital to give the two orbitals differing energies and an expected rhombic EPR spectrum. Single-crystal EPR spectral measurements for [Fe(TMP)  $(4-CNPy)(HIm)]ClO_4$  reveal a rhombic spectrum with g values of 3.05, 2.07 and 1.22. This clearly shows that the  $d_{xz}$  and  $d_{yz}$  orbitals are separated in energy.

With the available *g*-values for [Fe(TMP)(4-CNPy) (HIm)]ClO<sub>4</sub> the Taylor formalism [48] can now be used to evaluate the relative energies of the three lowest *d* orbitals. These values, expressed in terms of the energy of spin orbit coupling constant  $\lambda$  are shown on the right hand side of Fig. 6. For comparison, the energies of a bis-ligated 1-methylimidazole complex is shown at the left [6]. Although the energy difference between the  $d_{xx}$ 



Fig. 5. Steroscopic packing diagrams of the forms of  $[Fe(TMP)(4-CNPy)(HIm)]ClO_4$ . Top shows form A and the bottom shows form B



Fig. 6. Diagram showing the relative energies of the three lowest *d*-orbitals for  $[Fe(TMP)(4-CNPy)(HIm)]ClO_4$  (right) and a comparison complex (left)

and  $d_{yz}$  orbitals is slightly smaller in the mixed-ligand complex, the two orbitals are clearly still well-separated.

The axial bonding to iron was thus controlled using 4-CNPy as a strong  $\pi$  acceptor (poor base) with low affinity for the ferric porphyrinate, while HIm was used as a strong  $\pi$  donor (good base) with high affinity for the ferric porphyrinate. Thus the ligand pair chosen to obtain a synergic effect or a "push-pull" system was found to be a viable choice for a mixed axial ligand system.

### Summary

The reaction of [Fe(TMP)(OClO<sub>3</sub>)] with 6 equivalents of 4-CNPy followed by the addition of 1 equivalent of imidazole yields the mixed-ligand complex [Fe(TMP) (4-CNPy)(HIm)]ClO<sub>4</sub>. The two distinct ligands are found to have a relative perpendicular orientation that is consistent with a push–pull synergic effect of the strongly  $\pi$ -accepting ligand 4-CNPy and the  $\pi$  and  $\sigma$ donating imidazole ligand. This is also consistent with the Mössbauer and EPR spectra that show a classical ( $d_{xy}$ )<sup>2</sup>( $d_{xz}$ ,  $d_{yz}$ )<sup>3</sup> ground state.

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### **Supporting Information Available**

ORTEP and formal diagrams for form **B** (Figures S1 and S2) and the Mössbauer spectrum for [Fe(TMP)(4-CNPy)(1-AcIm)]ClO<sub>4</sub> (Fig. S3). Crystallographic details for both forms **A** and **B** (Tables S1–S11) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet. com/jpp/jpp.shtml. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC 1432125. Copies can be obtained on request, free of charge, *via* www.ccdc.cam. ac.uk/data\_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ ccdc.cam.ac.uk).

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- 12. Abbreviations used: Porphyrin Ligands: TMP, 5,10, 15,20-tetramesitylporphyrin dianion; TPP, tetraphenylporphyrin dianion; OEP, octaethylporphyrin OETPP, octaethyltetraphenylporphyrin dianion: dianion; TCl<sub>2</sub>PP, meso-tetra(2,6-dichlorophenyl) porphyrin dianion; Proto, protoporphyrin IX dianion; OMTPP, octamethyltetraphenylporphyrin dianion; TpivPP, picket fence porphyrin dianiom; TiPrP tetra(*i*-propyl)porphyrin dianion. Other Ligands: HIm, imidazole; 4-CNPy, 4-cyanopyridine; 1-AcIm, 1-acetylimidazole; 1-MeIm, 1-methylimidazole; 2-MeHIm, 2-methylimidazole; 3-ClPy, 3-chloropyridine; 4-NMe<sub>2</sub>Py, 4-dimethylaminopyridine; Py, pyridine; 5-MeHIm, 5-methylimidazole; BzHIm, 1-benzimidazole; Nax, axial nitrogen donor; N<sub>n</sub>, porphinato nitrogen.
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